Secondary Bonding. Part 8.[1] The Crystal and Molecular Structure of Diphenyl Telluroxide

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The crystal and molecular structure of diphenyl telluroxide has been determined by *X*-ray diffraction at room temperature. The crystals are monoclinic, space group *Cc*, with $a = 31.310(12)$, $b = 5.629(1)$, $c = 18.025(6)$ Å, $\beta = 139.18(1)°$, $U = 2\,076.7(10)$ Å^3, and $Z = 8$. The structure has been refined to a final R 0.038 for 1 910 independent reflections (four-circle diffractometer measurements). It consists of $Ph_2Te{=}O$ monomers [Te–C 2.137(average), Te=O 1.890 Å (average)] linked by short Te–O secondary bonds [Te–O 2.554 Å (average)] to give unsymmetrical dimers. Much longer interactions between dimers [Te · · · O 3.771 Å (average)] occupy the fifth positions of octahedra around each Te atom.

As part of a series of investigations into primary and secondary bonding in tellurium compounds we have prepared diphenyl telluroxide and determined its molecular structure. The isomorphous structures of the lighter homologues Ph_2MO (M = S or Se) have been determined (although not to present-day accuracy).[2] They both contain isolated molecules with M · · · O interactions that are either very long or non-existent. Replacing S or Se by Te would be expected to increase the strength of the intermolecular forces, and might lead to a completely different structural type, as in $(Ph_2IO)_n$, which is apparently an O-bridged polymer (discussed below). It is also of significance to discover whether any secondary bonds are of the linear X–Te · · · O form, or show the complex arrangements of Te · · · O interactions found in a series of organotellurium nitrates.[3]

EXPERIMENTAL

Preparation.—Ph_2TeO was prepared by dissolving Ph_2TeCl_2 in a slight excess of warm 10% aqueous NaOH containing a little methanol; the solution was filtered and deposited well formed crystals over a 24-h period. The crystals cannot be satisfactorily recrystallised; m.p. 192—194 °C (decomp.) (Found: C, 48.4; H, 3.5. Calc. for $C_{12}H_{10}OTe$: C, 48.4; H, 3.4%). The i.r. spectrum (Nujol mull between CsI plates) was recorded in the range 4 000—200 cm^{-1} on a Perkin-Elmer 580B spectrophotometer.

Crystal Data.—$C_{12}H_{10}OTe$, $M = 297.8$, Monoclinic, $a = 31.310(12)$, $b = 5.629(1)$, $c = 18.025(6)$ Å, $\beta = 139.18(1)°$, $U = 2\,076.7(10)$ Å^3, $D_m = 1.88$, $Z = 8$, $D_c = 1.90$ g cm^{-3}, $F(000) = 1\,066$, λ(Mo-K_α) = 0.710 69 Å, $\mu = 28.32$ cm^{-1}. The unit-cell parameters were obtained by least-squares fit to the position of 15 reflections in the range $25 < 2\theta < 30°$ using the standard program of a Syntex $P2_1$ diffractometer.

X-Ray Intensity Measurements.—Intensity data were collected by the θ—2θ scan technique with variable scan rates from 3.0 to 29.0° min^{-1} (in 2θ) and scan width ±1°. Stationary background counts were made with a time equal to half the scan time for each reflection. Three standard reflections were checked every 200 reflections to monitor the stability of the compound; there was a slight systematic decrease in F_o with time for which a correction was made. 2 574 Reflections with $2\theta < 50°$ were measured of which 1 910 independent reflections were considered observed [$I/\sigma(I) > 3.0$]. Lorentz and polarization corrections were applied to the data followed by an absorption correction using the program ABSCOR.[4] Systematic absences *hkl*, $h + k \neq 2n$ and *h*0*l*, $l \neq 2n$ correspond to space groups *Cc* (no. 9) or *C*2/*c* (no. 15).

Solution and Refinement of the Structure.—The three-

TABLE 1

Atomic co-ordinates ($\times 10^4$) for Ph_2TeO *

Atom	*X*	*Y*	*Z*
Te(1)	0	−2 829(2)	0
Te(2)	538.9(5)	1 505.5(17)	−573.9(8)
C(27)	997(5)	1 699(23)	−1 054(9)
C(28)	864(7)	−110(26)	−1 738(12)
C(29)	1 109(7)	98(31)	−2 107(12)
C(211)	1 577(7)	3 809(33)	−1 203(11)
C(212)	1 348(6)	3 719(30)	−799(11)
C(210)	1 456(7)	2 100(36)	−1 863(11)
C(21)	1 474(5)	1 329(20)	1 176(8)
C(22)	1 847(6)	−643(23)	1 536(8)
C(23)	2 467(7)	−852(26)	2 633(10)
C(24)	2 688(7)	933(27)	3 381(11)
C(25)	2 346(7)	2 900(32)	3 055(12)
C(26)	1 705(7)	3 136(27)	1 926(11)
C(11)	−929(6)	−3 474(25)	−1 710(9)
C(12)	−1 257(6)	−5 555(24)	−1 987(10)
C(13)	−1 872(7)	−5 873(27)	−3 128(13)
C(14)	−2 153(6)	−4 197(33)	−3 921(11)
C(15)	−1 794(7)	−2 198(37)	−3 631(13)
C(16)	−1 202(7)	−1 751(28)	−2 518(11)
C(17)	−394(5)	−3 070(29)	569(10)
C(18)	−271(6)	−4 921(24)	1 167(12)
C(19)	−505(7)	−5 038(31)	1 601(11)
C(110)	−902(6)	−3 101(24)	1 352(10)
C(111)	−1 010(7)	−1 276(29)	759(12)
C(112)	−747(7)	−1 199(21)	368(10)
O(11)	43(5)	490(32)	29(9)
O(21)	353(5)	−1 815(14)	−863(9)
H(12)	−1 058	−6 745	−1 419
H(13)	−2 107	−7 469	−3 348
H(14)	−2 595	−4 462	−4 684
H(15)	−1 993	−820	−4 256
H(16)	−951	−131	−2 251
H(18)	15	−6 163	1 366
H(19)	−384	−6 279	2 077
H(110)	−1 109	−3 243	1 581
H(111)	−1 263	107	586
H(112)	−839	220	−67
H(22)	638	−1 543	−1 874
H(23)	1 027	−1 141	−2 571
H(24)	1 594	2 093	−2 186
H(25)	1 832	5 130	−1 052
H(26)	1 419	5 000	−359
H(28)	1 652	−2 017	1 008
H(29)	2 745	−2 199	2 839
H(210)	3 083	727	4 142
H(211)	2 520	4 194	3 571
H(212)	1 431	4 451	1 675

* Estimated standard deviations are in parentheses in Tables 1—4.

dimensional Patterson function was consistent with two independent tellurium atoms in the non-centrosymmetric space group *Cc* but not with space group *C2/c*. A trial structure with these two Te atoms gave $R = 0.22$ after two cycles of positional and isotropic thermal refinement. The positions of the remaining non-hydrogen atoms were located by successive refinement and three-dimensional Fourier synthesis. Anisotropic thermal and positional least-squares refinement of all non-hydrogen atoms followed by difference-Fourier synthesis failed to reveal the hydrogen atoms which were therefore input in calculated positions with fixed isotropic temperature factors of 0.069 Å^2. An empirical weighting scheme was applied giving reduced weight to reflections of high and low sinθ and F_o. Final least-squares refinement gave $R = 0.038$, this being rather lower (and having more consistent bond lengths) than a refinement with the opposite hand ($R = 0.039$). All calculations were performed on a Burroughs B6700 computer using the '*X*-RAY 76' [5] suite of programs. Scattering factors were taken from ref. 6 in the analytical form. Table 1 contains the atomic co-ordinates and Table 2 bond lengths and angles. Structure factors and thermal parameters are listed in Supplementary Publication No. SUP 23235 (15 pp.).*

TABLE 2

Bond lengths (Å) and angles (°) in Ph_2TeO

Te(1)–O(11)	1.871(18)	Te(2)–O(21)	1.909(8)
Te(1)–C(11)	2.127(9)	Te(2)–C(21)	2.133(8)
Te(1)–C(17)	2.122(23)	Te(2)–C(27)	2.165(21)
Te(1)–O(21)	2.563(21)	Te(2)–O(11)	2.545(22)
Te(1) · · · O(11′)	3.762(18)	Te(2) · · · O(21′)	3.780(8)
Te(1) · · · Te(2)	3.537(2)	Te(2) · · · Te(1′)	4.090(2)
C(11)–C(12)	1.38(2)	C(21)–C(22)	1.37(2)
C(12)–C(13)	1.41(2)	C(22)–C(23)	1.37(2)
C(13)–C(14)	1.34(2)	C(23)–C(24)	1.38(3)
C(14)–C(15)	1.38(3)	C(24)–C(25)	1.33(3)
C(15)–C(16)	1.38(2)	C(25)–C(26)	1.42(1)
C(16)–C(11)	1.38(2)	C(26)–C(21)	1.38(2)
C(17)–C(18)	1.33(2)	C(27)–C(28)	1.40(2)
C(18)–C(19)	1.42(4)	C(28)–C(29)	1.35(3)
C(19)–C(110)	1.44(3)	C(29)–C(210)	1.39(3)
C(110)–C(111)	1.33(3)	C(210)–C(211)	1.34(3)
C(111)–C(112)	1.43(4)	C(211)–C(212)	1.36(4)
C(112)–C(17)	1.36(2)	C(212)–C(27)	1.40(2)

O(11)–Te(1)–C(11)	101.6(5)
O(11)–Te(1)–C(17)	96.1(8)
C(11)–Te(1)–C(17)	91.8(6)
O(21)–Te(1)–C(11)	84.4(6)
O(21)–Te(1)–C(17)	169.3(4)
O(21)–Te(1)–O(11)	74.9(7)
C(11)–Te(1) · · · O(11′)	81.1(4)
C(17)–Te(1) · · · O(11′)	87.5(6)
O(11)–Te(1) · · · O(11′)	175.4(6)
O(21)–Te(1) · · · O(11′)	101.8(4)
O(21)–Te(2)–C(21)	98.7(4)
O(21)–Te(2)–C(27)	95.6(7)
C(21)–Te(2)–C(27)	90.6(6)
O(11)–Te(2)–C(21)	87.5(6)
O(11)–Te(2)–C(27)	169.8(5)
O(11)–Te(2)–O(21)	74.8(7)
C(21)–Te(2) · · · O(21′)	98.4(4)
C(27)–Te(2) · · · O(21′)	88.5(4)
O(21)–Te(2) · · · O(21′)	162.3(3)
O(11)–Te(2) · · · O(21′)	101.6(5)

Te(1)–O(11)–Te(2)	105.5(9)	Te(2)–O(21)–Te(1)	103.6(7)
Te(1)–C(11)–C(12)	119(1)	Te(2)–C(21)–C(22)	117(1)
Te(1)–C(11)–C(16)	118(1)	Te(2)–C(21)–C(26)	122(1)
Te(1)–C(17)–C(18)	122(2)	Te(2)–C(27)–C(28)	118(1)
Te(1)–C(17)–C(112)	118(1)	Te(2)–C(27)–C(212)	120(1)
C(11)–C(12)–C(13)	117(1)	C(21)–C(22)–C(23)	121(2)
C(12)–C(13)–C(14)	122(1)	C(22)–C(23)–C(24)	118(2)
C(13)–C(14)–C(15)	119(1)	C(23)–C(24)–C(25)	122(1)
C(14)–C(15)–C(16)	121(2)	C(24)–C(25)–C(26)	120(2)
C(15)–C(16)–C(11)	119(2)	C(25)–C(26)–C(21)	117(2)
C(16)–C(11)–C(12)	121(1)	C(26)–C(21)–C(22)	120(1)
C(17)–C(18)–C(19)	122(2)	C(27)–C(28)–C(29)	118(1)
C(18)–C(19)–C(110)	118(2)	C(28)–C(29)–C(210)	121(2)
C(19)–C(110)–C(111)	118(2)	C(29)–C(210)–C(211)	120(2)
C(110)–C(111)–C(112)	122(2)	C(210)–C(211)–C(212)	123(2)
C(111)–C(112)–C(17)	120(2)	C(211)–C(212)–C(27)	117(2)
C(112)–C(17)–C(18)	119(2)	C(212)–C(27)–C(28)	121(2)

RESULTS AND DISCUSSION

The structure (Figure 1) consists of dimers of Ph_2TeO with two shared O atoms between each pair of Te atoms, giving rise to four-co-ordination at each Te atom. The oxygen bridging is very unsymmetrical and each Te atom can best be described as forming one primary bond (mean 1.89 Å) and one secondary bond (mean 2.55 Å) to oxygen. This dimeric structure is similar to that adopted by Ph_2IX (X = Cl, Br, or I),[7] but in that series the halogen bridging is symmetrical and the I–X distances are much longer than for a single bond, so that the interpretation as $(Ph_2I^+X^-)_2$ held together by secondary bonds seems the most satisfactory. The presence of two lone pairs at each iodine atom in the latter also results in precisely planar dimers.

There are no other Te–O interactions less than the sum of the van der Waals radii (3.58 Å), the next shortest interactions being Te(1) · · · O(11′), 3.762(18) Å, and

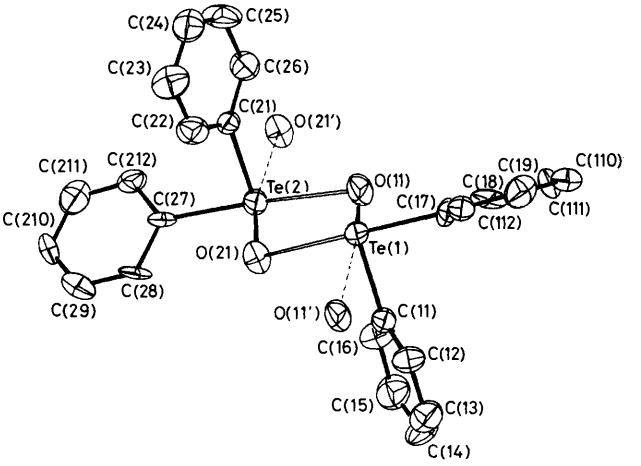


FIGURE 1 View of the molecule showing the atom numbering. The short secondary bond is shown in outline, and the long Te · · · O interaction is dotted

Te(2) · · · O(21′), 3.780(8) Å. Whilst these are very long they do complete a distorted square-based pyramidal geometry at each Te atom, as they are approximately *trans* to the shortest Te–O interactions. These very long secondary bonds give rise to weakly linked chains of dimers parallel to *b* (Figure 2). In Ph_2SO, the shortest intermolecular contact formed by S is in the same direction as these contacts by Te, but with a length of 4.2 Å, it cannot be regarded as significant. In the title compound, notably short Te · · · Te interactions [3.537(2) Å] occur

* For details, see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

within the dimers and another Te · · · Te interaction [4.090(2) Å] is found between dimers.

The oxygen bridging angles [105.5(9) and 103.6(7)°] are in accord with sp^3 hybridization at the oxygen and contrast with the more open angles found in essentially

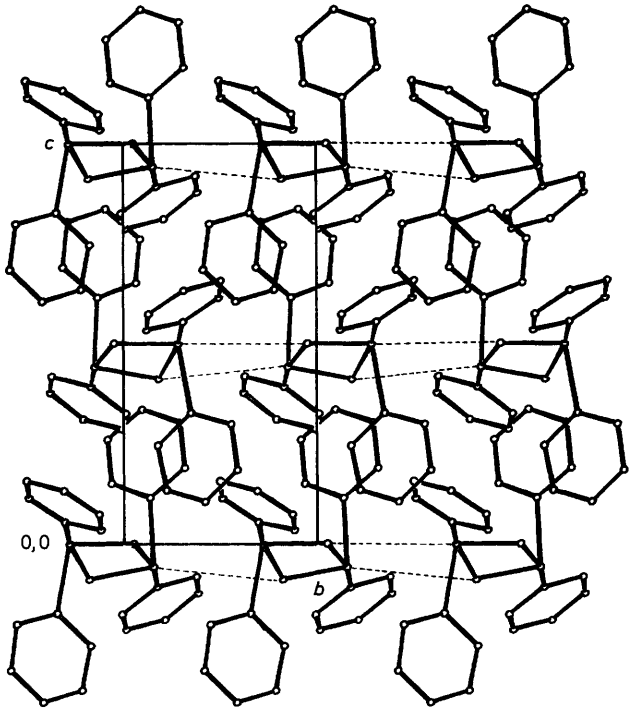


FIGURE 2 Packing diagram, viewed down *a*. The long Te · · · O interaction is dotted

symmetrically bridged basic tellurium nitrates,[3] $[PhI(NO_3)]_2O$,[8] and $[Ph_2Te(NCS)]_2O$ [9] (Table 3) where there may be some π interaction between the *p* orbitals of the oxygen atoms and the *d* orbitals of Te or I.

TABLE 3

Distances and angles around bridging oxygen atoms in Ph_2TeO and related compounds

Compound	Ref.	M–O (Å)	M–O–M(°)
PhTeO	This work	1.871(18), 2.563(21)	105.5(9) 103.6(7)
$[Ph_2Te(NO_3)]_2O{\cdot}Ph_2TeOH{\cdot}NO_3$	3	1.909(8), 2.545(27) 1.983(2), 1.971(3)	125.46(13)
$(PhTeO{\cdot}NO_3)_n$	3	1.983(3), 1.912(4), 2.015(3), 1.887(3)	121.42(19) 123.99(19)
$[Ph_2Te(NCS)]_2O$	9	1.985(4)	121.7(4)
$[PhI(NO_3)]_2O$	8	1.96(5) 2.05(5)	123.7(6)

The structure contrasts with that adopted by the lighter homologue Ph_2SO (and presumably by the isomorphous Se compound).[2] Comparison of the bond angles reveals that the sulphoxide and by inference the selenoxide are more tetrahedral in shape than the telluroxide (Table 4), suggesting more *s* orbital participation in the bonding of the S and Se compounds than in that of the telluroxide. It is also possible to regard the interaction with the bridging oxygen as the donation of an extra electron pair to Te, which should then have pseudo-trigonal bipyramidal geometry. However, if this model

TABLE 4

Comparative angles (°) around M in the compounds Ph_2MO

	M = Te	M = S
C–M–O	101.6(5)	106.2(7)
	96.1(8)	106.2(7)
	95.6(7)	
	98.7(4)	
C–M–C	91.8(6)	97.3(9)
	90.6(6)	

is correct, it is surprising to find one axial and one equatorial phenyl group, and although the equatorial angles C(11)–Te–O(11) and C(21)–Te–O(21) are the largest of those observed, they are much smaller than the 120° which would be anticipated.

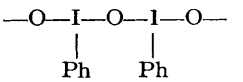
TABLE 5

Infrared absorption frequencies (cm^{-1}) of Ph_2TeO

Band		Assignment
732s	C_6H_5	C–H out of plane deformation
722s		
711 (sh) *	Te=O	asymmetric stretch
695s	C_6H_5	C–H out-of-plane deformation
688s		
658m	Te=O	symmetric stretch
612w		
468s	Te–C	stretch
442s		
312s	Te=O	bend
289s		
240m	Te–O · · · Te	bend (?)
225m		

* Overlapped by C–H deformation.

As well as the contrast with Ph_2SO, a significant contrast emerges between Ph_2TeO and iodosylbenzene, PhIO. No direct structural evidence is available for the latter, because it is insoluble in all solvents with which it does not react. Its i.r. spectrum [10] shows four frequencies apart from those of the benzene ring: 538, 446, 415, and 294 cm^{-1}. Notably, these do not include any frequency comparable to the 760—790 cm^{-1} expected for I=O. By contrast, the i.r. spectrum of Ph_2TeO (Table 5) shows two absorptions at relatively high frequency, 711 and 658 cm^{-1}, which can be attributed to Te=O stretching vibrations. A structure for iodosylbenzene of the type shown below accounts for its insolubility and



allows assignment of the i.r. spectrum as 538 cm^{-1}, I–O–I asymmetric stretch; 446 cm^{-1}, I–C stretch; 415 cm^{-1}, I–O–I symmetric stretch; 294 cm^{-1}, I–O–I

bend(?). The chemical inference is that the increasing M–O interactions seen in the sequence M = S, Se, and Te is greater still with M = I.

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